

Multiple anion formation in low energy electron collisions with Tl atoms: Regge-pole prediction

A. Z. Msezane and Z. Felfli
*Center for Theoretical Studies of Physical Systems,
 Clark Atlanta University, Atlanta, Georgia 30314 USA*

D. Sokolovski
*School of Mathematics and Physics, Queen's University of Belfast, Belfast, BT7 #1NN, United Kingdom
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The complex angular momentum (CAM) calculated low-energy $0 \leq E \leq 5\text{eV}$ electron elastic total cross section (TCS) for In is benchmarked through its recently measured electron affinity (Walter *et al.*, Phys. Rev. A **82**, 032507 (2010)). The TCSs for Tl and Ga atoms are then calculated using the CAM method. From the dramatically sharp resonances in the TCSs binding energies for Tl^- and Ga^- negative ions formed during the collisions are extracted and compared with existing values. Three stable bound negative ions of Tl are predicted.

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Recently, Walter *et al.* [1] have measured using infrared photodetachment threshold spectroscopy the electron affinity (EA) of In to be 383.92(6) meV. This value, important for benchmarking theory, compares very well with most theoretical EAs [2-7] but differs substantially from previous measurements [8, 9]. For the Tl atom the calculated EAs [3-5] differ significantly from the measured ones [8, 10] while for Ga the agreement among the theoretical EAs is generally good, but the theoretical EAs [3-6] deviate substantially from the experimental values [8, 11]. The recently observed excellent catalytic properties of Au and Pd nanoparticles and the exceptional catalytic activity of the Au-Pd catalyst when catalyzing H_2O_2 [12] have provided a new impetus to study low-energy electron elastic scattering from atoms in general, in search of nanocatalysts [13]. To our knowledge, there are no electron scattering cross sections for the In, Tl and Ga atoms available in the literature within the electron impact energy range of interest in the present work.

In this paper we explore low-energy $E < 5.0\text{eV}$ elastic collisions between an electron and the complex atoms In, Tl and Ga through the calculation of the elastic total cross sections (TCSs) and search for long-lived resonances. These, if they exist, are manifestations of the formation of stable weakly bound ground and excited negative ions as resonances [14, 15]. The choice of Tl and Ga is based on the fact that these are isoelectronic to In and may help in understanding the behavior of electronic affinities along isoelectronic sequences. From the energy positions of the characteristic resonances we extract the binding energies (BEs) of the ground and the excited negative ions formed during the collisions. The recent complex angular momentum (CAM) or Regge-pole methodology [16, 17] is used in the investigations; it requires no *a priori* knowledge of the experimental or other theoretical data as inputs. The imaginary part of the CAM, $\text{Im } L$, is used to distinguish between the shape resonances (short-lived resonances) and the stable bound states of the negative ions (long-lived resonances) formed

as Regge resonances in the electron-atom collisions.

Crucial to the existence and stability of most negative ions are the mechanisms of electron-electron correlations and core-polarization interactions. In the CAM description of scattering we use the Mulholland formula wherein is embedded the former effects in the form [16, 17] (atomic units are used throughout)

$$\sigma_{tot}(E) = 4\pi k^{-2} \int_0^\infty \text{Re}[1 - S(\lambda)] \lambda d\lambda - 8\pi^2 k^{-2} \sum_n \text{Im} \frac{\lambda_n \rho_n}{1 + \exp(-2\pi i \lambda_n)} + I(E) \quad (1)$$

where S is the scattering matrix, $k = \sqrt{2mE}$, with m being the mass, ρ_n the residue of the S-matrix at the n^{th} pole, λ_n and $I(E)$ contains the contributions from the integrals along the imaginary λ -axis. contribution has been demonstrated to be negligible [21]. We will consider the case for which $\text{Im } \lambda_n \ll 1$ so that for constructive addition, $\text{Re } \lambda_n \approx 1/2, 3/2, 5/2 \dots$, yielding $l = \text{Re } L \cong 0, 1, 2 \dots$. The importance of Eq. (1) is that a resonance is likely to affect the elastic TCS when its Regge pole position is close to a real integer [17].

The calculation of the elastic TCSs and the Mulholland partial cross sections uses the Thomas-Fermi (T-F) type model potential in the well investigated form [22]

$$U(r) = \frac{-Z}{r(1 + aZ^{1/3}r)(1 + bZ^{2/3}r^2)}, \quad (2)$$

where Z is the nuclear charge and a and b are adjustable parameters. For small r , the potential describes the Coulomb attraction between an electron and a nucleus, $U(r) \sim -Z/r$, while at large distances it mimics the polarization potential, $U(r) \sim -1/(abr^4)$ and accounts properly for the vital core-polarization interaction at very low energies. The effective potential

$$V(r) = U(r) + \frac{L(L+1)}{2r^2} \quad (3)$$

is considered here as a continuous function of the variables and L . The potential, Eq. (2) has been used successfully with the appropriate values of a and b . When the TCS as a function of b has a resonance [21] corresponding to the formation of a stable bound negative ion, this resonance is longest lived for a given value of the energy which corresponds to the electron affinity of the system (for ground state collisions). This was found to be the case for all the systems we have investigated thus far. This fixes the optimal value of b for Eq. (2). The optimal value of a was found to be 0.2 for the three atoms considered here. In the study of low-energy electron scattering from Cu atoms, it was demonstrated that the ground and excited states are polarized differently [23] as expected. This explains the use in this paper of different values for the optimal parameter b for the ground and excited atoms.

The calculation of the TCSs and the Mulholland partial cross sections is described in [21]. Briefly, two independent approaches are adopted. The first integrates numerically the radial Schrödinger equation for real integer $l = ReL$ values of L to sufficiently large r values. The S -matrix is then obtained and the TCSs are evaluated as the traditional sum over partial waves, with the index of summation being l . The second part calculates the poles positions and residues of the S -matrix, $S(L, k)$, following a method similar to that of Burke and Tate [24]. In the method the two linearly independent solutions, f_L and g_L , of the Schrödinger equation are evaluated as Bessel functions of complex order and the S -matrix, which is defined by the asymptotic boundary condition of the solution of the Schrödinger equation, is thus evaluated. Further details of the calculation may be found in [24].

ImL is important in distinguishing between the shape resonances (short-lived resonances) and the stable bound, both ground and excited, states of the negative ions (long-lived resonances) formed as Regge resonances in the electron-atom scattering [21]. In the definitions of Connor [25] and the applications [21] the physical interpretation of ImL is given. It corresponds inversely to the angular life of the complex formed during the collision. A small ImL implies that the system orbits many times before decaying, while a large ImL value denotes a short-lived state. For a true bound state, namely $E < 0$, $ImL = 0$ and therefore the angular life, $1/[ImL] \rightarrow \infty$, implying that the system can never decay. ImL is also used to differentiate subtleties between the bound and the excited states of the negative ions formed as resonances during the collisions.

I. RESULTS

Figure 1 presents the elastic TCS for In. Near threshold the curve is characterized by a Ramsauer-Townsend (R-T) minimum at 0.0662 eV and a shape resonance at 0.236 eV. Immediately following the shape resonance, the

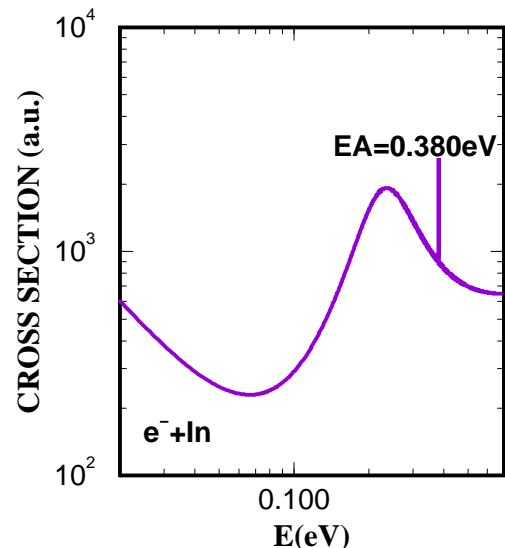


FIG. 1: Elastic TCS (a.u.) for In atoms showing the R-T minimum and the shape resonance followed by the dramatic resonance at 0.380 eV, corresponding to the EA of In.

very sharp resonance at 0.380 eV corresponds to the negative ion formed during the collision of the electron and the ground state In atom and defines the EA of In. The value compares excellently with the latest measurement [1] and calculation [4]. The TCS curve typifies many such TCSs that have already been calculated, such as those of the lanthanide atoms.

Thus, the complex angular momentum calculated low-energy $0 \leq E < 0.7$ eV electron elastic total cross section for In is benchmarked to the recent measurement [1] through the electron affinity. Henceforth the CAM method will be used to calculate the electron elastic scattering cross sections for Tl and Ga. From the TCSs the binding energies (BEs) of the resultant negative ions of Tl^- and Ga^- formed during the collisions as resonances will be extracted and compared with existing values.

Figure 2 contrasts the low-energy $0 \leq E < 5$ eV electron-Tl elastic scattering TCSs for the ground state, curve (a) and excited states, curves (b) and (c). The structure of each curve is significantly different from that of the other. This is indicative of the importance of the electron-electron correlations and core-polarization interactions in the electron-Tl scattering, at both the ground and the excited states levels. In the energy region of the structures, the ground state cross section is characterized by a R-T minimum at 0.733 eV followed by a shape resonance at 1.141 eV and then by a deeper and broader second minimum at about 2.193 eV. The very sharp resonance right in the minimum corresponds to the stable bound state of the Tl^- negative ion formed during the collision as a Regge resonance and determines the EA of Tl; its value is 2.415 eV. Most significant here is that the EA of Tl is very close to those of Au and Pt [26] and its TCS resembles those of Au and Pt as well. This con-

figuration of resonances and minima in the elastic TCS, typified by those of the Au and Pt TCSs, represents a signature of good nanocatalysts [27]. Perhaps, Tl can replace Au or Pt as a possible nanocatalyst in some situations and reduce the costs significantly. This calls for immediate experimental investigation.

Curves (b) and (c) represent electron scattering TCSs for excited Tl atoms, resulting in the formation of Tl^- negative ions. The sharp curves with binding energies (BEs) of 0.281 eV and 0.0664 eV correspond respectively to Tl^- ions in their first and second excited states. A very important revelation in the comparison is the appearance of the bound state resonances of the negative ions together with the shape resonances of the ground and the excited states. Both theoretical calculations and experimental measurements could easily mistake one for the other. This could also be problematic in the use of the Wigner threshold law in high precision measurements of BEs of valence electrons using photodetachment threshold spectroscopy. Furthermore, the determination of the R-T minimum of the ground state could be hindered since it is mixed in together with the cross sections for the excited states.

Indeed, the misidentification is evident in the comparison of the available theoretical and experimental EAs of Tl, presented in Table II. For Tl the EA values of 0.27 eV [3] and 0.291 eV [4] compare excellently with our calculated binding energy of 0.281 eV. Since our EA for Tl is 2.415 eV, we conclude that these theoretical values correspond to the BE of an excited Tl^- anion and not to the EA as claimed. So, the EA values of Tl reported by the various calculations and measurements presented in Table II do not correspond to the EA; they are the BEs of the first excited state of the Tl^- anion. The various calculations agree reasonably well with one another and with the experiment [10], although it has a large error margin.

In figure 3 the TCS for the electron-Ga scattering is presented. This curve resembles that of the first excited state TCS for Tl. It is characterized by the usual shape resonance, followed by a dramatically sharp resonance which corresponds to the bound state of the Ga^- negative ion formed during the collision. The BE of the negative ion is determined to be 0.222 eV which can be compared with the data in Table II. Ref. [3] has the EA of Ga as 0.29 eV, while the experiment [8] has the value 0.30 ± 0.15 eV. Both our value and the other theoretical one [3] agree reasonably well with each other and with the experiment, although it has a large error margin.

Our extracted BEs from the resonances in the TCSs of In, Tl and Ga atoms are tabulated in Table I and in Table II where they are compared with other theoretical calculations and measurements.

We have benchmarked the CAM calculated TCS for the electron-In scattering through the recently measured EA [1]. Our EA agrees excellently with that of the measurement and the calculated value [3]. The CAM method has then been used to evaluate the TCSs for the elec-

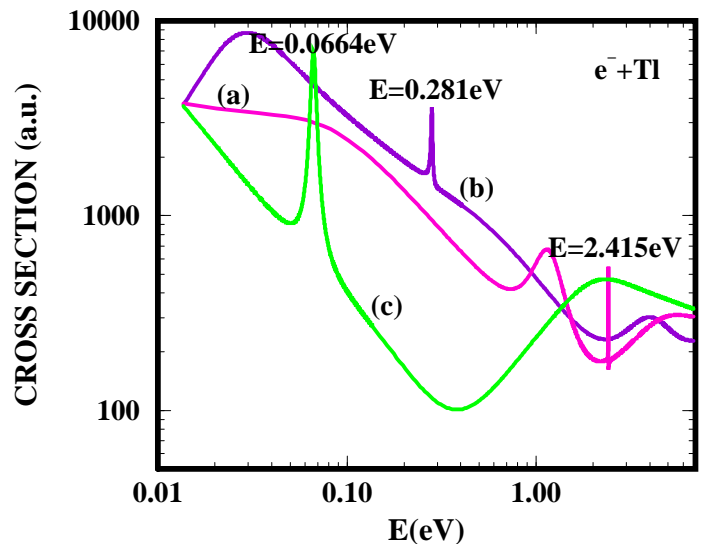


FIG. 2: Total cross sections (*a.u.*) for electron elastic scattering from Tl atoms versus E (eV), are contrasted. The curves (a), (b) and (c) represent respectively the ground state, first excited state and second excited state. All the curves are characterized by very sharp resonance structures corresponding to the formation of Tl^- negative ions during the collisions. Note that for the ground state curve the position of the bound state of the Tl^- anion is at the second minimum.

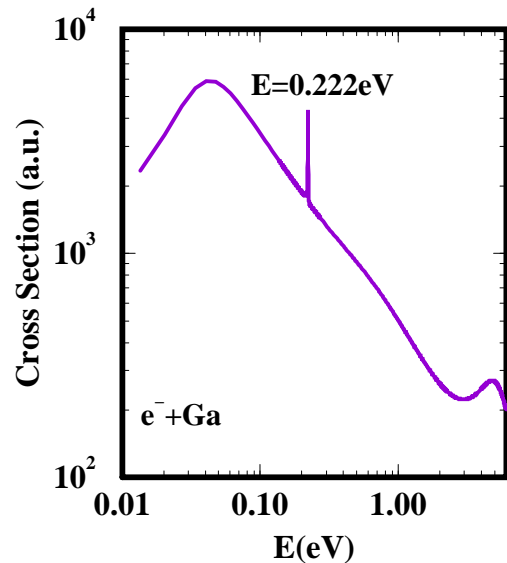


FIG. 3: Elastic TCS (*a.u.*) for Ga atoms showing the shape resonance followed by the dramatic resonance, corresponding to a bound state of the Ga^- anion.

tron scattering from Tl and Ga atoms. Binding energies for electron attachment to the ground state of Tl and when the Tl atom is excited have been extracted from the TCSs and compared with the available data. Our calculated BE for the first excited state of the Tl^- negative ion agrees excellently with the EAs of Refs. [3,

TABLE I: Calculated binding energies, BEs (eV), shape resonances, SRs (eV) and minima, 1st and 2nd min. (eV) for In, Tl and Ga atoms.

Z	Atom	State	1st min.	SR	2nd min.	BE
49	In	ground	0.0662	0.236	—	0.380
81	Tl	ground	0.733	1.141	2.193	2.415
		1 st excited	—	0.0295	—	0.281
		2 nd excited	0.503	—	—	0.0664
31	Ga	ground	—	0.0407	—	0.222

TABLE II: Measured and calculated EAs (eV) for In, Tl and Ga are compared with the present calculated binding energies, BEs (eV).

Z	Atom	EA, expt.	EA, theory	BE, this work
49	In	0.38392(6) [1] 0.30 ± 0.20 [8] 0.404(9) [9]	0.371 [2] 0.380 [3] 0.393 [4] 0.419 [5] 0.374 [6] 0.403 [7]	0.380
81	Tl	0.377(13) [10] 0.20 ± 0.20 [8]	0.27 [3] 0.291 [4] 0.40 ± 0.05 [5]	0.0664, 0.281, 2.415
31	Ga	0.30 ± 0.15[8] 0.43(3) [11]	0.29 [3] 0.305 [4] 0.301 [5]a 0.297(13) [6]	0.222

4] and reasonably well with the EA measured by [10]. However, our calculated EA for the Tl atom is 2.415 eV. Consequently, the theoretical and the experimental EAs for Tl in the published literature actually correspond to the BE of the first excited state of the Tl⁻ negative ion. This calls for immediate experimental verification.

We also conclude from the configuration of the resonances and minima in the TCSs for Tl that Tl promises to be a good nanocatalyst (see Ref. [27] for discussions), capable of replacing Au and/or Pt in some applications. This also calls for experimental investigation. Finally, we predict the formation as resonances of three stable bound states of the Tl⁻ negative ion during the collision of a slow electron with Tl atoms; the TCSs for Tl are similar to those of the Ag atom [27].

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